INORGANIC COMPOUNDS

Acta Cryst. (1995). C**51**, 175–177

Hydroxylammonium Scandium Sulfate Sesquihydrate, $Sc(NH_3OH)(SO_4)_2.1.5H_2O$

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(*Received* 23 *September* 1993; *accepted* 24 *March* 1994)

Abstract

The crystal of $Sc(NH_3OH)(SO_4)_2.1.5H_2O$ is built up from scandium, sulfate and hydroxylammonium ions, and from two crystallographically different molecules of water. The structure can be described as comprising chains of octahedrally and tetrahedrally arranged O atoms around Sc and S atoms, respectively. These chains are hydrogen bonded by the hydroxylammonium ions and the water molecules.

Comment

The X-ray structure determination of the title compound was undertaken as part of a project focused on the structural studies of double sulfate compounds of the transition elements. Previously reported crystallographic data concerning the scandium double sulfates of the type MSc$(SO_4)_2$ (where M = Na, K, Rb, Cs or NH_4) are rather poor. These compounds have been obtained in microcrystalline form and because of this the structural data have been determined mainly from X-ray powder photographs (Bashkov, Komissarova, Spiridonov & Shatskij, 1972; Koritnaya & Pokrovskij, 1980). The crystal and molecular structures of scandium double sulfate compounds have only been given for $Na_3Sc(SO_4)_3.5H_2O$ (Sizova, Voronkov & Belov, 1974).

The structure of the compound presented in this work consists of scandium, sulfate and hydroxylammonium ions, and two crystallographically different molecules of water. One of the water molecules is bonded to Sc; the other, having an occupancy of 0.5, is close to a centre of symmetry and is hydrogen bonded to O(9) of the hydroxylammonium ion as well as to O(5) of the sulfate ion.

The Sc atom is octahedrally coordinated by five O atoms from the sulfate groups and by one water molecule, O(10). The values of the Sc—O bond distances vary between 2.026 (2) and 2.130 (2) Å. These distances compare well with the average values found for previously determined data concerning six-coordinated Sc (Anderson, Neuman & Melson, 1973; Hansson, 1973; Valkonen, Niinisto, Eriksson, Larsson & Skoglund, 1975; Valkonen, 1978). The most distant atom from Sc is O(10) of the coordinated water molecule. This is also the case in some sulfate compounds of the rare earths (Dereigne, Manoli, Pannetier & Herpin, 1972; Larsson, Linderbrandt, Niinisto & Skoglund, 1973). The octahedron around the metal is distorted and the O—Sc—O angles vary between 84.11 (7) and 96.45 (7)°. The geometries of the hydroxylammonium and sulfate ions are as expected (Vilminot, Anderson & Brown, 1973; Tanaka & Tsujikawa, 1982; Ishakova, Gasanov, Bondar, Kleinman, Novik & Trunov, 1988).

Both types of water are involved in hydrogen bonding. The water molecule coordinated to the Sc atom is hydrogen bonded to the sulfate ion. The statistically distributed water molecule has contacts with the O atoms of

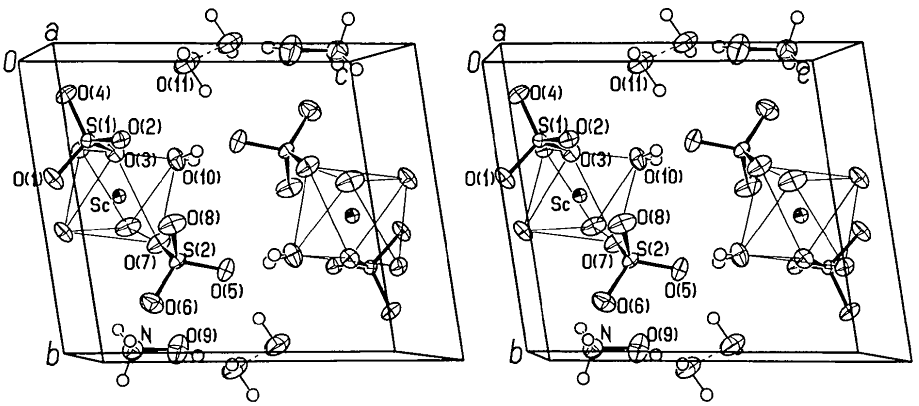

Fig. 1. Stereoscopic view of the unit cell together with the atom-labelling scheme.

Acta Crystallographica Section C
ISSN 0108-2701 © 1995

the sulfate and hydroxylammonium groups. All O atoms of the two sulfate ions except O(4) are involved in hydrogen bonding. This seems to be the reason for the short S—O(4) bond distance.

Fig. 1 presents a stereoscopic view of the unit cell together with the atom-labelling scheme used. The octahedra and tetrahedra are connected in chains along the *a* axis. These chains are hydrogen bonded in the *b*-axis direction with each hydroxylammonium ion, as well as with each statistically disordered water molecule, and in the *c*-axis direction with each Sc-coordinated water molecule.

Experimental

Crystals were grown from an aqueous solution of $Sc_2(SO_4)_3$ and $(NH_3OH)_2SO_4$ in a 1:1 molar ratio. Well shaped crystals were obtained by recrystallization from the water solution, which was heated and then cooled slowly. The density D_m was measured by flotation in tribromomethane and tetrachloromethane.

Crystal data

$Sc(NH_3OH)(SO_4)_2.1.5H_2O$
$M_r = 298.14$
Triclinic
$P\overline{1}$
$a = 5.123$ (1) Å
$b = 8.955$ (1) Å
$c = 10.147$ (1) Å
$\alpha = 80.93$ (1)°
$\beta = 75.36$ (1)°
$\gamma = 89.17$ (1)°
$V = 444.6$ (2) $Å^3$
$Z = 2$
$D_x = 2.227$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 90 reflections
$\theta = 10$–18°
$\mu = 1.322$ mm^{-1}
$T = 293$ (1) K
Approximate prism
0.54 × 0.36 × 0.28 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2659 measured reflections
2604 independent reflections
1935 observed reflections [$I > 3\sigma(I)$]

$\theta_{max} = 30°$
$h = 0 \rightarrow 7$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 141 reflections
intensity decay: 1.9%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.034$
$S = 0.42$
2166 reflections
137 parameters
H-atom parameters not refined
$w = W_f W_s$ (see below)

$(\Delta/\sigma)_{max} = 2.33$
$\Delta\rho_{max} = 0.14$ e $Å^{-3}$
$\Delta\rho_{min} = -0.19$ e $Å^{-3}$
Extinction correction: Larson (1967)
Extinction coefficient: 0.7 (1)
Atomic scattering factors from Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sc	0.13936 (7)	0.46155 (4)	0.22313 (4)	0.0140 (2)
S(1)	0.71644 (9)	0.29136 (5)	0.08829 (5)	0.0143 (2)
S(2)	0.58531 (9)	0.68536 (5)	0.30453 (5)	0.0172 (2)
O(1)	0.7595 (4)	0.4150 (2)	−0.0299 (2)	0.0294 (9)
O(2)	0.9447 (3)	0.2962 (2)	0.1530 (2)	0.0234 (7)
O(3)	0.4668 (3)	0.3216 (2)	0.1900 (2)	0.0225 (7)
O(4)	0.6997 (4)	0.1450 (2)	0.0493 (2)	0.0308 (8)
O(5)	0.5478 (5)	0.7152 (2)	0.4455 (2)	0.037 (1)
O(6)	0.6660 (4)	0.8198 (2)	0.2030 (2)	0.0346 (9)
O(7)	0.3230 (3)	0.6256 (2)	0.2947 (2)	0.0328 (9)
O(8)	0.7836 (4)	0.5653 (2)	0.2796 (2)	0.0363 (9)
O(9)	0.0994 (6)	0.9854 (3)	0.3315 (3)	0.051 (1)
N	0.1610 (5)	0.9856 (3)	0.1891 (2)	0.032 (1)
O(10)	0.0395 (4)	0.3324 (2)	0.4250 (2)	0.0282 (8)
O(11)†	0.555 (1)	0.0364 (5)	0.4250 (6)	0.047 (2)

† Occupancy factor = 0.5.

Table 2. *Selected bond lengths* (Å) *and hydrogen-bond distances* (Å)

Sc—O(3)	2.070 (2)	S(1)—O(1)	1.472 (2)
Sc—O(7)	2.072 (2)	S(1)—O(2)	1.483 (2)
Sc—O(10)	2.130 (2)	S(1)—O(3)	1.478 (2)
Sc—O(2^{i})	2.104 (2)	S(1)—O(4)	1.437 (2)
Sc—O(8^{i})	2.026 (2)	S(2)—O(5)	1.461 (2)
Sc—O(1^{ii})	2.038 (2)	S(2)—O(6)	1.446 (2)
		S(2)—O(7)	1.486 (2)
O(9)—N	1.399 (4)	S(2)—O(8)	1.475 (2)

D—H···*A*	*D*···*A*
N—H(1)···O(6^{i})	2.918 (3)
N—H(2)···O(6)	2.987 (3)
N—H(3)···O(2^{ii})	2.982 (3)
O(9)—H(4)···O(11^{iii})	2.799 (7)
O(10)—H(5)···O(5^{iv})	2.970 (3)
O(10)—H(6)···O(5^{v})	2.753 (4)
O(11)—H(7)···O(9^{vi})	2.767 (6)
O(11)—H(8)···O(5^{v})	2.737 (6)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x - 1, 1 + y, z$; (iii) $x, 1 + y, z$; (iv) $-x, 1 - y, 1 - z$; (v) $1 - x, 1 - y, 1 - z$; (vi) $1 + x, y - 1, z$.

Maximum $\Delta/\sigma = 2.33$ is at extinction, next highest $\Delta/\sigma = 0.11$ [at U_{22}(Sc)], average $\Delta/\sigma = 0.035$. $w = W_f W_s$, where $W_f(F_o < 10.0) = (F_o/10.0)^{1.5}$, $W_f(F_o > 18.0) = (18.0/F_o)^{1.4}$, $W_f(10.0 < F_o < 18.0) = 1.0$, and $W_s(\sin\theta < 0.35) = (\sin\theta/0.35)^{2.8}$, $W_s(\sin\theta > 0.43) = (0.43/\sin\theta)^{0.7}$, $W_s(0.35 < \sin\theta < 0.43) = 1.0$, was applied to keep $\Sigma w(F)^2$ uniform over the ranges of F_o and $(\sin\theta)/\lambda$. Computer programs: *XRAY76* (Stewart *et al.*, 1976).

The financial support of the Ministry of Science and Technology of the Republic of Slovenia is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and hydrogen-bonding data have been deposited with the IUCr (Reference: AB1121). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Anderson, T. J., Neuman, M. A. & Melson, G. A. (1973). *Inorg. Chem.* **12**, 927–930.

Bashkov, B. I., Komissarova, L. N., Spiridonov, F. M. & Shatskij, V. M. (1972). *Vestn. Mosk. Univ. Khim.* **5**, 598–600.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Dereigne, A., Manoli, J.-M., Pannetier, G. & Herpin, P. (1972). *Bull. Soc. Fr. Mineral. Cristallogr.* **95**, 269–280.
Hansson, E. (1973). *Acta Chem. Scand.* **27**, 2841–2851.
Ishakova, L. D., Gasanov, J. M., Bondar, C. A., Kleinman, I. A., Novik, B. K. & Trunov, B. K. (1988). *Neorg. Mater.* **24**, 998–1003.
Koritnaya, F. M. & Pokrovskij, A. N. (1980). *Vestn. Mosk. Univ. Khim.* **21**, 390–392.
Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
Larsson, L. O., Linderbrandt, S., Niinisto, L. & Skoglund, U. (1973). *Suom. Kemistil. B*, **46**, 314–322.
Sizova, R. G., Voronkov, A. A. & Belov, N. V. (1974). *Dokl. Akad. Nauk. SSSR*, **217**, 1073–1076.
Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System*. Technical Report TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, USA.
Tanaka, M. & Tsujikawa, I. (1982). *Acta Cryst.* B**38**, 2793–2797.
Valkonen, J. (1978). *Acta Cryst.* B**34**, 3064–3066.
Valkonen, J., Niinisto, L., Eriksson, B., Larsson, L. O. & Skoglund, U. (1975). *Acta Chem. Scand. Ser. A*, **29**, 866–872.
Vilminot, S., Anderson, M. R. & Brown, I. D. (1973). *Acta Cryst.* B**29**, 2628–2630.

Acta Cryst. (1995). C**51**, 177–179

FeAl$_3$Si$_2$

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(*Received* 25 *March* 1994; *accepted* 3 *August* 1994)

Abstract

The title compound, iron trialuminium disilicide, is isotypic with PdGa$_5$, but presents a superstructure. All the crystals investigated were found to be twinned by pseudosymmetry. The average structure was refined in the space group *I4/mcm*. Then the superstructure was solved in *Pbcn*. It can be described as a succession of layers parallel to (001), made up of distorted bicapped tetragonal prisms, Al(1)Fe$_2$Al(2)$_4$Si$_4$, centred on Al(1). Each of these polyhedra is connected by sharing edges with four similar polyhedra of the same layer and by Fe-corner sharing with two polyhedra of the adjacent layers.

Comment

FeAl$_3$Si$_2$ is a minor phase in ferrosilicon alloys that contain about 65 wt% Si and 1–4 wt% Al. Its crystal structure was investigated as part of a study of the alloy microstructure.

The existence of FeAl$_3$Si$_2$ was reported by Takeda & Mutuzaki (1940). Panday & Schubert (1969) found the compound to be tetragonal with a = 6.07 and c = 9.50 Å, isotypic with PdGa$_5$ (Schubert, Lukas, Meissner & Bahn, 1959). Westgren, quoted by Panday & Schubert (1969), noted the presence of superstructure reflections which suggested order between Al and Si atoms. In fact, the formula FeAl$_3$Si$_2$ is a nominal one since the composition extends over a rather large range: the data of Zarechnyuk, German, Yanson, Rykhal & Muraveva (1981), Rivlin & Raynor (1981) and Anglézio (1990), along with our own electron microprobe analysis results, indicate the following composition ranges, expressed in

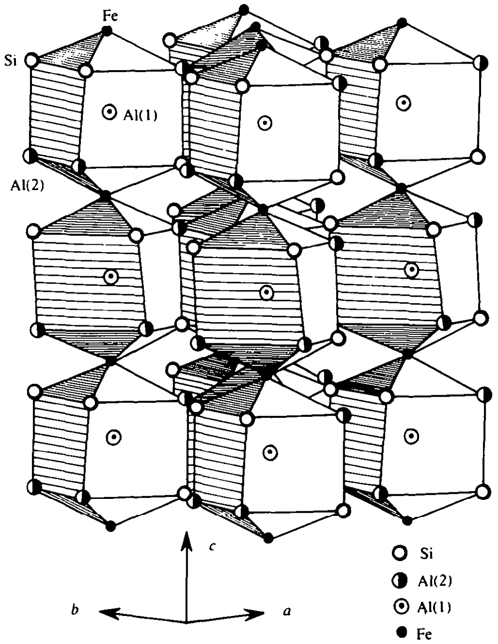

Fig. 1. Crystal structure of FeAl$_3$Si$_2$ viewed as an arrangement of Al-centred polyhedra.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995